MEASURING CELL FOR ION CYCLOTRON RESONANCE SPECTROMETER

This invention relates to a measuring cell for an Ion Cyclotron Resonance (ICR) spectrometer.

Fourier Transform Ion Cyclotron Resonance is a technique for high resolution mass spectrometry which employs a cyclotron principle.

One such FT-ICR spectrometer is shown in our co-pending Application No. GB 0305420.2 which is incorporated herein by reference in its entirety. As is described in that application, ions generated in an ion source (usually at atmospheric pressure) are transmitted through a system of ion optics employing differential pumping and into an ion trap. Ions are ejected from the trap, through various ion guides and into a measurement cell. In that cell, the field lines of a homogeneous magnetic field (generated by an external superconducting magnet, for example), extend along the cell in parallel with the cell's longitudinal axis. By applying an r.f. field, perpendicular to the magnetic field, the ions can be excited so as to produce cyclotron resonance. Charged particles in the cell then orbit as coherent bunches along the same radial paths but at different frequencies. The frequency of the circular motion (the cyclotron frequency) is proportional to the ion mass. A set of detector electrodes are provided and an image current is induced in these by the coherent orbiting ions. The amplitude and frequency of the detected signal are indicative of the quantity and mass of the ions. A mass spectrum is obtainable by carrying out a Fourier

Transform of the 'transient', i.e. the signal produced at the detector's electrodes.

Figure 1a shows, highly schematically, the arrangement of electrodes in a prior art cell. In particular, a section through a cell 10 is shown, along with its longitudinal axis z. An orthogonal section through the cell 10 is also shown in Figures 1d and 1e which show, respectively, the electrode arrangements in a cylindrical and in a square rectangular configuration respectively.

In Figure 1a, the cell 10 comprises a central excitation electrode 20 and outer excitation electrodes 30, 40 surrounding that. An r.f. voltage is applied to each of the excitation electrodes so as to produce an excitation field, and a d.c. voltage is applied to the outer electrodes 30, 40 so as to provide a trapping field. In an alternative arrangement to that shown in Fig. 1a, capacitors may be situated between the RF and DC connections.

The trapping field created by the prior art arrangement of Figure 1a is shown in Figure 1b.

The longitudinal ("z") axis of Figure 1b is intended to be generally to the same scale as that of Figure 1a, so that the magnitude of the trapping field U in the z-direction of Figure 1b corresponds with the position along the z axis of the electrodes in Figure 1a. Figure 1b also shows the approximate range of the homogeneous field region of the applied magnetic field.

Figure 1c shows a schematic representation of equipotentials of the excitation field in the cell 10 of Figure 1a. It will be seen that the excitation field

equipotentials are generally parallel to the z axis in the centre of the cell and close to the 'z' axis, so that there is no excitation electric field component in the z direction, but curve significantly so that there is a non-zero excitation electric field component in the z-direction (see Figure 1g). Optimal excitation for FTMS requires an homogeneous electrical excitation field. R.f. electric field components in the radial direction of the cell cause the ions to gain energy in that (desired) radial direction. Any finite electrical excitation field component in the direction of the cell's longitudinal axis 'z' causes an acceleration in that axial direction. Longitudinal acceleration of ions is undesirable because the potential barrier in that direction is typically only of order 1 eV (higher trapping potentials causing unwanted field distortion) and so ions may easily escape from the cell and thus be lost.

One theoretical possibility to remove the axial r.f. field components towards the edges of the cell would be to make the electrodes of infinite length. The problem with this is that, as the electrodes become longer in the z-direction, so the ions reside in a volume that extends outside of the homogeneous zone of the magnetic field. This in turn causes a reduction in the resolving power of the spectrometer.

An alternative approach to the production of an excitation electric field with parallel field lines is described in US-A-5,019,706. Here, additional electric r.f. signals are applied to one or more of the trapping electrodes on both sides of the measuring cell. This causes the inhomogeneities in the field lines at the cell

extremities (as a result of its finite length in the axial direction) to be balanced out by heterodyning with the additional r.f. field components which are introduced by the trapping electrodes, so that the ions in the trap experience an r.f. field more like that which would be produced by a cell of infinite axial length. Lines of equipotential in the cell of US-A-5,019,706 are shown for the purposes of illustration only, in Figure 1f.

Nevertheless, the arrangement of US-A-5,019,706 suffers from the disadvantage that electrodes have to share the static trapping potential and the RF excitation potentials, which may increase the cost of the driving electronics and/or the amount of noise. Furthermore, the potential well which traps ions in the cell extends as far as the region of excitation field curvature in this arrangement so that trapped ions still experience an inhomogeneous excitation field, as may be seen from Figure 1f.

Against this background, there is provided, in a first aspect, a measurement cell for an FTMS spectrometer, comprising: an excitation electrode arrangement positioned about a longitudinal axis which extends in a direction generally parallel to the field direction of an applied homogeneous magnetic field; and a trapping electrode arrangement, also positioned about the said longitudinal axis, for trapping ions longitudinally in the cell within a trapping region defined by the trapping electrode arrangement; wherein at least a part of the excitation electrode arrangement extends axially outwardly of the trapping region defined by the trapping electrode arrangement.

Placing at least a part of the excitation electrode arrangement axially outwardly of the trapping region causes the non-linear region of the excitation field to be "pulled" axially outwards relative to the prior art arrangements so that the field lines are more linear in the region axially between the trapping electrodes in which the ions are confined, which defines the trapping region, and where, in preference, the magnetic field is homogeneous.

In accordance with one preferred embodiment, the excitation electrode arrangement comprises a central excitation electrode part, and outer excitation electrode parts, the outer excitation electrode parts being positioned axially outwardly of the trapping electrode arrangement. The excitation electrode parts may be linked by wires, or may alternatively be connected by relatively narrow bridge members that extend axially between a first outer excitation electrode and the central excitation electrode, and between a second outer excitation electrode and the central excitation electrode, respectively. In that case, the trapping electrode arrangement may comprise a first trapping electrode, located in an aperture defined by the axially inner edge of the first outer excitation electrode part, a first axially outer edge of the central excitation electrode part, and two circumferentially displaced axially extending narrow bridge members, and a second trapping electrode located in an aperture defined by the axially inner edge of the second outer excitation electrode part, a second axially outer edge of the central excitation electrode part, and two further

circumferentially displaced, axially extending narrow bridge members.

In an alternative embodiment, the excitation electrode arrangement comprises a relatively narrow strip extending substantially the length of the cell. In that case, the trapping electrode arrangement is circumferentially displaced from the excitation electrode strip, and may be aligned with, and/or interspersed with, one or more detection electrodes. In this case, it is desirable that the excitation electrode arrangement is relatively narrow, as this avoids excessive disturbance of the trapping field, that is, maintains the trapping field's homogeneity. The term "relatively narrow" may be narrow relative to the length (in the longitudinal axis direction) of the trapping electrode arrangement, or narrow compared to the detection electrode arrangement, or both. Additionally or alternatively, the excitation electrode arrangement may be elongate, again in the longitudinal axial direction, in order to maximise the amount of the trapping region within the homogeneous excitation field provided by the excitation electrode arrangement.

In accordance with a further aspect of the present invention, there is provided method of trapping and exciting ions in a measurement cell of an FTMS spectrometer, the method comprising: (a) applying a magnetic field to the measurement cell so as to produce a region of homogeneous magnetic field, having a magnetic field direction, within the cell; (b) applying a d.c. trapping potential to a plurality of trapping electrode arrangement positioned about a longitudinal axis which

extends in a direction generally parallel to that magnetic field direction, so as to trap ions in the cell, in that axial direction within a trapping region defined by the trapping electrode arrangement; and (c) applying an r.f. excitation potential to an excitation electrode arrangement positioned about that longitudinal axis, so as to resonantly excite the ions in the cell, at least a part of the excitation electrode arrangement extending axially outwardly of the trapping region defined by the trapping electrode arrangement; wherein the ions are trapped within the region of homogeneous magnetic field and wherein the ions are further trapped within a homogeneous region of an excitation electric field generated by the application of the r.f. excitation potential to the said excitation electrodes.

In still a further aspect of the present invention, there is provided a method of trapping and exciting ions in a measurement cell of an FTMS spectrometer, the method comprising: (a) applying a magnetic field to the measurement cell so as to produce a region of homogeneous magnetic field, having a magnetic field direction, within the cell; (b) applying a d.c. trapping potential to a plurality of trapping electrodes which are arranged symmetrically about a longitudinal axis which extends in a direction generally parallel to that magnetic field direction, so as to trap ions in the cell, in that axial direction; and (c) applying an r.f. excitation potential to a plurality of excitation electrodes which are arranged symmetrically about that longitudinal axis, so as to resonantly excite the ions in the cell, at least a part of the excitation electrodes being arranged

axially outwardly of the trapping electrodes; wherein the ions are trapped within the region of homogeneous magnetic field and wherein the ions are further trapped within a homogeneous region of an excitation electric field generated by the application of the r.f. excitation potential to the said excitation electrodes. The invention also extends to a measurement cell for an FTMS spectrometer, comprising: a plurality of excitation electrodes arranged symmetrically about a longitudinal axis which extends in a direction generally parallel to the field direction of an applied homogeneous magnetic field; and a plurality of trapping electrodes, also arranged symmetrically about the said longitudinal axis; wherein at least some of the excitation electrodes are arranged axially outwardly of the trapping electrodes.

Further preferred features are set out in the dependent claims which are appended hereto.

The invention may be put into practice in a number of ways and some preferred embodiments will now be described by way of example only and with reference to the accompanying drawings, in which:

Figure 1a shows a schematic longitudinal section through a prior art FTMS measurement cell;

Figure 1b shows, to the same scale as Figure 1a, the d.c. trapping potential U along the longitudinal axis z of the cell of Figure 1a;

Figure 1c shows, again to the same scale as Figure 1a, lines of r.f. excitation equipotential τ along the longitudinal axis z of the cell of Figure 1a;

Figures 1d and 1e show views along the line AA of Figure 1a, for circular and square section cells respectively;

Figure 1f shows lines of r.f. excitation potential τ along the longitudinal axis of the measurement cell of US-A-5,019,706 which also forms a part of the state of the art;

Figure 1g shows the electrical field components of an arbitrary point on an r.f. excitation field equipotential of the cell of Figure 1a, towards the edges of that cell, along with an indication of the radial and axial components of force thereby applied to an ion at that point;

Figure 2a shows a schematic longitudinal section through an FTMS measurement cell in accordance with a first embodiment of the present invention;

Figure 2b shows, to the same scale as Figure 2a, the d.c. trapping potential U along the longitudinal axis z of the cell of Figure 2a;

Figure 2c shows, also to the same scale as Figure 2a, lines of equipotential for the r.f. excitation field τ along the longitudinal axis z of the cell of Figure 2a;

Figure 3a shows a schematic longitudinal section through an FTMS measurement cell in accordance with a second embodiment of the present invention;

Figure 3b shows, to the same scale as Figure 3a, lines of equipotential for the r.f. excitation field τ along the longitudinal axis of the measurement cell of Figure 3a;

Figure 4 shows a schematic longitudinal section through an FTMS measurement cell in accordance with a third embodiment of the present invention

Figure 5 shows still a further embodiment of an FTMS measurement cell in accordance with the present invention, with the trapping electrodes being formed as inserts in the extended excitation electrodes;

Figure 6 shows another embodiment of an FTMS measurement cell according to the present invention, with the trapping electrodes interlaced with the detection electrodes and elongate, narrow excitation electrodes;

Figure 7a shows a side view of another embodiment of an FTMS measurement cell according to the present invention; and

Figure 7b shows a section along the line AA' of Figure 7a.

Turning first to Figure 2a, a schematic longitudinal section through an FTMS measurement cell 100 in accordance with a first embodiment of the present invention is shown. The cell 100 is rotationally symmetrical about a longitudinal axis z and may, for example, be cylindrical or oblong in shape, as will be explained further below.

The cell 100 comprises a first pair of central excitation electrodes 110 which are located about an axially central point of the cell 100. Axially outward of this central pair of excitation electrodes 110, on either side thereof, are two pairs of trapping electrodes 120, 130. The trapping electrodes of Figure 2a have the same, or similar, diameter, to the first pair of excitation electrodes 110.

Axially outwardly of the pairs of trapping electrodes 120, 130 are second and third pairs of outer excitation electrodes 140, 150 respectively. Again, the diameter of these outer excitation electrode pairs is the same or similar to that of the trapping and central excitation electrode pairs. Thus, the outer electrode pair 140 and the central electrode pair 110 'sandwich' the trapping electrode pair 120 between them, and the outer electrode pair 150 and central electrode pair 110 'sandwich' the trapping electrode pair 130 between them.

An r.f. voltage supply 160 is connected, in the embodiment of Figure 2a, to each of the excitation electrode pairs 110, 140, 150. Although a single r.f. voltage supply (of a given voltage) may be attached to each of the excitation electrode pairs, different voltages and/or frequencies may instead be applied to each by virtue of voltage and/or frequency divider(s) respectively, or by using separate r.f. voltage supplies.

A d.c. voltage 170 is applied to the trapping electrodes 120, 130. Again, the same or different d.c. voltages may be applied to the two pairs of trapping electrodes 120, 130.

Figure 2b shows a schematic plot of the trapping field, U, as a function of axial position z. It will be seen that, in comparison with the prior art arrangement of Figure 1b, the trapping field has two clearly defined peaks 180 which coincide with the axial positions of the trapping electrodes 120, 130. The peaks then tail off sharply as the position z moves further away from the centre of the cell 100.

Figure 2c shows a schematic of the lines of equipotential of the excitation field generated in the cell 100 of Figure 2. It will be noted that the field lines are relatively flat and parallel with the z axis, across the bulk of the region of confinement of the ions which is between the two peaks 180 of the trapping potential U (Figure 2b). There is a small perturbation 190 in the excitation field in the region of the trapping electrodes, as is seen in Figure 2c, but this has not been found to affect the overall trapping and excitation unduly.

The arrangement of Figure 2a accordingly "pulls" the non-linear region of the excitation field outwards relative to the arrangement of Figure 1a so that the excitation electric field is essentially homogeneous in the trapping region. It will also be noted that the axial barriers formed by the peaks 180 in the trapping field coincide with the homogeneous area of the magnetic field (cf US-A-5,019,706, described above, where the (physical) axial barriers for trapped ions are in that case outside the homogeneous area of the magnetic field). Thus, high resolution FTMS measurements can be made (because a large proportion of trapped ions experience homogeneous magnetic and excitation fields) whilst the number of ions lost after injection into the cell 100 is minimized.

Although not shown in Figures 2a, 3a or 4, it will be understood that the cell 100 of Figure 2 also includes detecting electrodes which may (as in the arrangements of Figure 1d or 1e) be radially interspersed with the trapping and excitation electrodes. The detecting electrodes and the trapping/excitation electrodes may be

radially equally spaced from the axis z, so as to retain symmetry. In terms of the relative dimensions, the typical arrangement has excite electrodes that each occupy approximately one quarter of the circumference of the cell (the detection electrodes occupying most of the remaining two quarters of the circumference). Other ratios are, however, possible/desirable and these will be explored below.

Figure 3a shows an alternative arrangement of a measurement cell 100' to that of Figure 2a. Features common to these two Figures are nevertheless labelled with like reference numerals. In the cell 100' of Figure 3a, instead of connecting the r.f. voltage supply 160 only to the excitation electrodes 110, 140, 150, it is also connected, along with the d.c. voltage 170 to the trapping electrodes 120, 130. The logical layout of electrode potentials is shown in the upper part of Figure 3a. The physical layout, indicating one way of wiring the electrodes is shown in the lower part of that Figure. It will be seen that the r.f. and d.c. voltage supplies 160, 170 are decoupled from one another by employing a capacitance 200 between the r.f. and d.c. supplies to the trapping electrodes 120, 140, so that d.c. is not also supplied via the r.f. electrical leads to the excitation electrodes 110, 140, 150. Applying a combined d.c. and r.f. field in this way reduces the presence of the perturbation 190 in the vicinity of the trapping electrodes, as may be seen from Figure 3b which shows lines of equipotential in the cell 100' of Figure 3a.

Turning next to Figure 4, a further embodiment of a cell 100" for FTMS is shown. Again, the components common

to Figures 2a, 3a and 4 are labelled with like reference numerals. In the arrangement of Figure 4, each of the electrodes 110, 120, 130, 140 and 150 is selectively connectable to a.c. and d.c. voltages which are decoupled using capacitances 200. This allows for maximum flexibility. For example, each of the electrodes can first be energized with d.c. only, when the cell is first filled with ions. Thus, a trapping field can be established which has boundaries extending right to the edges of the cell 100". This trapping field can then be adjusted so as to squeeze the ions towards the centre of the cell 100"; in particular, the d.c. voltage can be adjusted on the electrodes so as to shift the potential well towards the centre of the cell 100" until there is no more d.c. voltage on the outer excitation electrodes 140, 150 or on the central excitation electrodes 110, and the trapping field resembles that of Figure 2b. At that point, the r.f. voltage supply 160 can be applied to the excitation electrodes 110, 140, 150 to arrive at the configuration of Figure 2a, or it may be applied to all of the electrodes, excitation plus trapping, to arrive at the configuration of Figure 3a. Other static field configurations may be envisaged as a precursor to the preferred trapping/excitation arrangements.

As may be seen in particular in Figure 2a, the excitation electrodes 110, 140, 150 are linked by a common connection to the r.f. voltage supply 160, about the annular trapping electrodes 120, 130. An alternative to this arrangement is shown in Figure 5, wherein the connections between the central excitation electrode 110 and the outer electrodes 140, 150 are formed by employing

a single piece electrode with narrow bridges 210 between the central excitation electrode part 110 and the two outer electrode parts 140, 150. It will be understood that Figure 5 shows a side view and that there is in fact a pair of the composite electrodes (formed from the central and outer parts 110, 140, 150 as linked by the bridges 210), but that only one of the pair is visible in the side view of Figure 5.

As a consequence of the bridges 210, part of the trapping is achieved by locating trapping electrode pairs 120, 130 in apertures 220 defined by the axially outer edges of the central excitation electrode 110, the axially inner edges of the outer electrode parts 140, 150 (each in the 'z' axis direction as shown in the Figure), and the bridges 210. The field generated by the arrangement of Figure 5 is otherwise the same as that shown in Figure 2c.

As can be seen in the side view of Figure 5, the circumferential space between the two sets of excitation electrodes 120, 140, 150 (only one of which pair is visible in Figure 5) has further electrodes for trapping and detection. In particular, trapping electrodes 230b, 230d are aligned with the trapping electrodes 120, 130 in the longitudinal direction of the cell so as to define a trapping volume that is axially between the electrodes 230b, 120 and the electrodes 230d, 130. Detection electrodes 230c are located axially between the trapping electrodes 230b, 230d. In the arrangement of Figure 5, further electrodes 230a, 230e are connected to DC (and usually, ground potential) since the ions in the measurement cell are trapped by the trapping field

axially inwardly of this and so there is little benefit in trying to detect with the electrodes 230a, 230e.

A further development of the arrangement of Figure 5 is shown in Figure 6. Here, the bridges 210 of Figure 5 are extended along the length of the cell, but the remaining parts of the excitation electrodes are discarded to leave narrow excitation electrode strips 300. The part of the excitation electrodes 110, 140, 150 extending around the major proportion of the circumference in Figure 5 is instead replaced in the embodiment of Figure 6 with detection electrodes 230c axially bounded with trapping electrodes 120, 130. As with the arrangement of Figure 5, there are also electrodes 230a, 230e outside of the trapping electrodes (in the longitudinal direction) but, again because the trapping region is defined between the trapping electrodes 120, 130, the outer electrodes are not usefully useable as detection electrodes and are accordingly connected to DC (usually, ground potential).

The arrangement of Figure 6 is based upon several principles. Firstly, the trapping field becomes distorted when the share of the trapping electrodes on the circumference decreases. This in turn reduces the quality of the detect signal produced from the detection electrodes 230c. However it has been realized that the trapping electrodes do not need to be interlaced with the excitation electrodes, and can instead be interlaced with the detection electrodes. Secondly, it has traditionally been understood that reducing the circumferential extent of the excitation electrodes below about 25% (i.e. below about 90°) would be a problem, since the smaller the

radial width (i.e. circumferential extent) of the excitation electrodes, the higher the required power. By employing power amplifiers matched to the high impedance of the measurement cell, rather than standard "off the shelf" amplifiers matched to 50Ω output as at present, the necessary power output is significantly reduced, thus enabling a reduction in excitation electrode width. For example, at 50Ω output impedance, a 100V excitation amplitude requires $V^2/Z=200$ Watts of output power. At 250Ω output impedance, only 40 Watts of power is needed. Indeed, maintaining narrow excitation electrodes in such an arrangement proves to be desirable, since this avoids significant disturbance of the trapping field. In general terms, when the trapping electrodes are interlaced with the excitation electrodes (Figures 2-5), it is desirable to keep the width of the excitation electrodes (i.e. the distance around the circumference of the measurement cell) below the length (in the axial or 'z' direction of the cell) of the trapping electrodes, in order to minimize the effect of the disturbance of the trapping field.

Figure 7a shows a side view of a measurement cell in accordance with still a further embodiment of the present invention. Figure 7b shows a sectional view through a section AA' of the cell of Figure 7a. As seen best in Figure 7b, the arrangement is relatively simple and contains only two pairs of electrodes. Two excitation electrodes 300_1, 300_2 extend in the z direction along the length of the measurement cell (Figure 7a), but extend radially (direction θ in Figure 7b) around only a small fraction of the 360° circumference of the cell. The

excitation electrodes are thus narrow but elongate. A pair of detection electrodes 230_1, 230_2 form most of the remainder of the circumference, but do not extend along the full length of the cell. Instead the detection electrodes 230_1 and 230_2 extend along the middle part of the cell in the z direction (Figure 7a) but are bounded by left and right trapping electrodes 120_1, 130_1 and 120_2, 130_2 respectively.

The wide angle occupied by the detection electrodes 230_1, 230_2 cause harmonics to arise in the detection signal obtained. These harmonics may however be removed by signal processing.

Although some specific embodiments of the invention have been described, it will be understood that these are by way of example only and that various modifications are possible. For example, whilst in Figures 3a and 4, the r.f. and d.c. voltages are decoupled using a capacitance, an inductance may be employed instead or as well. Furthermore, although only two pairs of outer excitation electrodes have been described, additional outer excitation electrodes may be employed, so as further to reduce inhomogeneities in the excitation field in the region of the homogeneous magnetic field. Indeed, interlaced trapping/excitation/trapping/excitation arrangements may also be employed.

As a further refinement, the cell 100, 100′ and 100″ may be fitted with end caps (not shown) that are located at either end of the cell, adjacent the outer excitation electrode pairs 140, 150 and which are mounted coaxially with the electrodes. Preferably, these end caps have a radius somewhat less than that of the excitation and

trapping electrodes so that the cell is only partially physically closed by the end caps. This arrangement permits the field shape to be controlled still further.

As still a further alternative, the central excitation electrode pair 110 may have a different diameter and/or may not be coaxial with the adjacent trapping electrode pairs 120, 130 or the outer excitation electrodes 140, 150. This allows for compensation for the excitation field in the vicinity of the trapping electrodes, once again so as to remove or at least reduce the magnitude of the perturbation 190 (Figure 2c).